Benzyl ether: a dynamic covalent motif for designing a trans-ether based covalent adaptable network (CAN)

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Experimental Section:

Chemicals and Materials:

Mesitol, trimethylolpropane and 2-(2-methoxyethoxy)ethanol (MEE) were purchased from BLD Pharm. Sodium methoxide, triethylene glycol (TEG), and p-toluenesulfonic acid were purchased from Avra Synthesis. n-Butanol, 1-hexanol, hydrochloric acid, anhydrous sodium sulfate, anisole and methanol were purchased from FINAR. Formaldehyde (36 – 40 %), sodium chloride, and potassium carbonate were purchased from MERCK. Sulfuric acid was purchased from RANKEM. Hydrobromic acid in water (~48 %), tetrahydrofuran (THF) and toluene were purchased from SRL chemicals. Chloroform, 1,4-dioxane, DCM and acetonitrile were purchased from Qualigens. Pentamethylbenzene (PMB) was purchased from TCI. Phthalic anhydride was purchased from CDH. Unless otherwise stated, all chemicals are used in their received form.

Instrumentation:

Nuclear Magnetic Resonance (NMR): The ¹H NMR and ¹³C NMR studies were carried out with a JEOL Delta (ECS) 400 MHz (100 MHz for ¹³C) spectrometer using CDCl₃ as a solvent at room temperature. Tetramethylsilane (TMS) was used as an internal standard, and the chemical shifts were represented in parts per million (ppm). The NMR data was processed using MestReNova software.

Attenuated Total Reflectance - Fourier Transform InfraRed: ATR -IR spectra were obtained on Perkin-Elmer 1000 UATR spectrometer at room temperature at a nominal resolution of 2 cm⁻¹ in the spectral range of 4000 cm⁻¹ to 500 cm⁻¹.

ESI-MS: Mass spectrometric data were obtained using Agilent of Premier-ESI-MS.

Gel Permeation Chromatography: Molecular weight and polydispersity index of linear polymer in THF solvent system was carried out using SHIMADZU RID-20A, LC-20AD, CTO-20AC. The instrument was calibrated using polystyrene standards. Samples were run with flow rate of 1 ml/min.

Thermogravimetric Analysis (TGA): TGA was performed using the Mettler Toledo SDTA851e instrument under an N₂ atmosphere at the heating rate of 10 °C/min, ranging from room temperature to 800 °C.

Differential Scanning Calorimetry (DSC): DSC studies were performed using TA instrument DSC2-00918 in the temperature -50 °C to 200 °C with a heating and cooling rate of 10 °C/min. The glass transition temperature (Tg) was taken as the midpoint of the endotherm of the second cycle.

Mechanical Reprocessing: Using a Polymer Press Techno Search (PF-M15) instrument equipped with a custom steel mold, the grounded network was shaped into rectangular thin films ($30 \times 8 \times 1 \text{ mm}$) (L x W x D) and a circular disk with a thickness of 1.5 mm and a diameter of 8 mm. The process of compression molding was conducted at a temperature of 170 °C under a constant pressure of 10 tons.

Tensile Measurement: Tensile tests were performed using the LLOYD Universal Testing Machine (Model EZ50) equipped with a 2000 N load cell. Rectangular bars with dimensions $30 \times 8 \times 1$ mm (L x W x D) were used for all the tests. All tests were carried out with a crosshead speed of 0.5 mm/min.

Rheological Measurements: Stress-relaxation studies were performed using an Anton Paar MC302e rheometer with parallel plate geometry containing a plate diameter of 8.0 mm and thickness of 1.5 mm over the temperature range of 140 °C to 170 °C. All the samples were subjected to thermal conditioning at 170 °C prior to the experiment. A constant 5% step strain rate and normal force between 0-5 N were maintained throughout the experiment.

Synthetic Procedure:

Synthesis of 1-Bromobutane: 10 g (134.91 mmol) of n-Butanol was taken in hydrobromic acid in water (54.58 g, 674.58 mmol) and heated at 80 °C for 24 hours with continuous stirring. The reaction mixture was cooled to room temperature, which resulted in the formation of two layers. The top layer was separated and dried over sodium sulfate to obtain the product with a 92 % yield (17.06 gm).

¹H NMR (δ ppm, CDCl₃, 400 MHz): 3.41 – 3.38 (t, 2H); 1.85 – 1.78 (m, 2H); 1.47 – 1.41 (m, 2H); 0.93 – 0.89 (t, 3H). ¹³C NMR (δ ppm, CDCl₃, 100 MHz): 34.84, 33.77, 21.38, 13.25.

Synthesis of 3,5-bis(chloromethyl)-2,4,6-trimethyl phenol (BCM-TMP): 10 g (73.52 mmol) Mesitol was taken in 1000 mL of two necks round bottom flask containing 300 mL of 1,4-Dioxane and stirred at room temperature. 200 mL of hydrochloric acid (35-38 %) and 210 mL of formaldehyde were added to it. The reaction mixture was purged with instantaneously prepared hydrochloric acid using sodium chloride and sulfuric acid. Subsequently, water is added, which results in the precipitation of the product. The precipitate was filtered and dissolved in chloroform. The chloroform layer was washed with water, passed through the sodium sulfate, and concentrated under vacuum to obtain the solid product with 70 % yield (11.98 g).

¹H NMR (δ ppm, CDCl₃, 400 MHz): 4.66 (s, 4H); 4.63 (s, 1H); 2.42 (s, 3H); 2.31 (s, 6H). ¹³C NMR (δ ppm, CDCl₃, 100 MHz): 150.33, 133.10, 129.09, 123.99, 41.68, 14.68, 12.05. ESI-MS: Calculated for $C_{11}H_{14}Cl_2O$ (232.0422): Observed: 197.0728 [M-Cl]⁺

Synthesis of 3,5-bis(methoxymethyl)-2,4,6-trimethyl phenol (BMM-TMP): 8.14 g (150.86 mmol) Sodium methoxide was taken in 100 mL of dry methanol and stirred at room temperature under nitrogen environment. 5 g (21.55 mmol) **BCM-TMP** dissolved in dry methanol and added to it, and the reaction mixture was heated at 50 °C for 12 hours with constant stirring. The reaction mixture was cooled to room temperature. 20 mL of cold water was added to it, followed by 100 mL of the HCI: H₂O (1:1). The mixture was washed with chloroform (3 x 70 mL). The separated organic layer was collected and concentrated to obtain a yellowish solid product with an 88 % yield (4.23 g).

¹H NMR (δ ppm, CDCl₃, 400 MHz): 4.44 (s, 4H); 3.38 (s, 6H); 2.33 (s, 3H); 2.21 (s, 6H). ¹³C NMR (δ ppm, CDCl₃, 100 MHz): 150.03, 132.65, 129.92, 124.17, 69.17, 58.11, 15.00, 12.19. ESI-MS: Calculated for $C_{13}H_{20}O_3$ (224.1412): Observed: 193.1227 [M-OCH₃]⁺

Synthesis of 1-butoxy-3,5-bis(methoxymethyl)-2,4,6-trimethylbenzene (BMM-TMB): 3.0 g (13.37 mmol) BMM-TMP, 5.49 g (40.12 mmol) 1-bromobutane, and 5.54 g (40.12 mmol) K_2CO_3 were taken in 60 mL acetonitrile and refluxed for 36 hours. The reaction mixture was cooled to room temperature, filtered, and concentrated to obtain the yellowish solid with a 93 % yield (3.48 g).

¹H NMR (δ ppm, CDCl₃, 400 MHz): 4.45 (s, 4H); 3.64 – 3.61 (t, 2H); 3.38 (s, 6H); 2.35 (s, 3H); 2.30 (s, 6H); 1.78 – 1.73 (m, 2H); 1.54 – 1.48 (m, 2H); 0.98 – 0.95 (t, 3H). ¹³C NMR (δ ppm, CDCl₃, 100 MHz): 154.01, 133.58, 133.45, 131.10, 72.62, 69.26, 58.18, 32.43, 19.48, 15.07, 14.09, 12.52. ESI-MS: Calculated for C₁₇H₂₈O₃ (280.2038): Observed: 279.1953 [M-H]⁺

Synthesis of 1-butoxy-3,5-bis(hexyloxy)methyl-2,4,6-trimethylbenzene (BBHM-TMB): 1.0 g (3.56 mmol) **BMM-TMB** was taken in 25 mL RB and heated to melt at 90 °C under a nitrogen environment, followed by the addition of 5 mol % of pTSA.H₂O. An excess of 1-hexanol (2.75 eq, 1.23 mL) was added to the reaction mixture and heated to 140 °C under a nitrogen environment for 23 hours. Subsequently,

the excess 1-hexanol was removed under reduced pressure to obtain the product, **BBHM-TMB**, with 92 % yield (1.38 g).

¹H NMR (δ ppm, CDCl₃, 400 MHz): 4.47 (s, 4H); 3.64 - 3.61 (t, 2H); 3.49 - 3.45 (t, 4H); 2.37 (s, 3H); 2.31 (s, 6H); 1.81 - 1.74 (m, 2H); 1.63 - 1.48 (m, 6H); 1.39 - 1.22 (m, 12H); 1.00-0.97 (t, 3H); 0.98 - 0.86 (t, 6H).

¹³C NMR (δ ppm, CDCl₃, 100 MHz): 154.06, 133.79, 133.60, 130.98, 72.64, 70.73, 67.65, 32.52, 31.83, 29.95, 26.10, 22.78, 19.65, 15.23, 14.20, 14.17, 12.60.

ESI-MS: Calculated for C₂₇H₄₈O₃ (420.3603): Observed: 438.3934 [M+NH₄]⁺



Figure S1: ¹H NMR spectra of 1-Bromobutane in CDCl₃.



Figure S2: ¹³C NMR spectra of 1-Bromobutane in CDCl₃.



Figure S3: ¹H NMR spectra of 3,5-bis(chloromethyl)-2,4,6-trimethylphenol (BCM-TMP) in CDCl₃.



Figure S4: ¹³C NMR spectra of 3,5-bis(chloromethyl)-2,4,6-trimethylphenol (BCM-TMP) in CDCl₃.



Figure S5: ESI-MS spectrum of compound 3,5-bis(chloromethyl)-2,4,6-trimethylphenol (BCM-TMB).



Figure S6: ¹H NMR spectra of 3,5-bis(methoxymethyl)-2,4,6-trimethylphenol (BMM-TMP) in CDCl₃.



Figure S7: ¹³C NMR spectra of 3,5-bis(methoxymethyl)-2,4,6-trimethylphenol (BMM-TMP) in CDCl₃.



Figure S8: ESI-MS spectrum of 3,5-bis(methoxymethyl)-2,4,6-trimethylphenol (BMM-TMP).



Figure S9: ¹H NMR spectra of 1-butoxy-3,5-bis(methoxymethyl)-2,4,6-trimethylbenzene (**BMM-TMB**) in CDCl₃.



Figure S10: ¹³C NMR spectra of 1-butoxy-3,5-bis(methoxymethyl)-2,4,6-trimethylbenzene (**BMM-TMB**) in CDCl₃.



Figure S11: ESI-MS spectrum of 1-butoxy-3,5-bis(methoxymethyl)-2,4,6-trimethylbenzene (**BMM-TMB**).



Figure S12: ¹H NMR spectra of 1-butoxy-3,5-bis((hexyloxy)methyl)-2,4,6-trimethylbenzene (**BBHM-TMB**) in CDCl₃.



Figure S13: ¹³C NMR spectra of 1-butoxy-3,5-bis((hexyloxy)methyl)-2,4,6-trimethylbenzene (**BBHM-TMB**) in CDCl₃.



Figure S14: ESI-MS spectrum of 1-butoxy-3,5-bis((hexyloxy)methyl)-2,4,6-trimethylbenzene (BBHM-TMB).

Model Study for the Dynamic Ether Exchange and Kinetics

The exchange reaction was performed between the hexyl derivative of mesitol (**BBHM-TMB**) and 2-(2methoxyethoxy)ethanol (**MEE**) using 5 mol% p-toluenesulfonic acid monohydrate (pTSA.H₂O) under solvent-free conditions (**Scheme S1**). **BBHM-TMB** (100 mg, 0.24 mmol) and pTSA.H₂O (2.26 mg, 0.0118 mmol) were taken in a 25 mL round bottom flask and kept under nitrogen purging for 10 minutes. To this, 12 equivalents of **MEE** (343 mg, 2.85 mmol) were added, and the reaction was set on a preheated oil bath at 130 °C under constant stirring. In order to monitor the reaction progress, aliquots were taken out from the reaction mixture at set time intervals and diluted with CDCl₃, which were immediately subjected to ¹H NMR spectroscopy at room temperature. The ¹H NMR spectra of the reaction mixture is shown in **Figure S15**. The intensity of the benzyl ether peaks of **BBHM-TMB**, denoted as 'a', and the benzyl ether peaks of **BBMEM-TMB**, denoted as 'c', were measured at various time intervals. The intensity of the 'a' peak decreased, while the intensity of the 'c' peak increased over time. This study also revealed that equilibrium is achieved in nearly 100 min at 130 °C (**Figure S17**).

Besides, to estimate the activation energy, the exchange reaction was carried out following the literature-reported methodologies.^{1–4} The reaction was carried at different temperatures ranging from 110 °C to 140 °C using a large excess of **MEE** (~30 eq. w.r.t **BBHM-TMB**). The use of excess **MEE** ensured that the reaction rate was independent of its concentration. The intensity of the benzyl ether peaks in **BBHM-TMB**, denoted as 'a', and the benzyl ether peaks of **BBMEM-TMB**, denoted as 'c', were measured at various time intervals. Since **BBHM-TMB** is bifunctional benzylic ether, the conversion was calculated based on the functional group conversion rather than the formation of the disubstituted product (**BBMEM-TMB**) or starting material (**BBHM-TMB**). The integral of the -CH₃ peak, the terminal methyl group attached to the butyl group in **BBHM-TMB**, was taken as a reference for the kinetic study, as the -CH₃ peaks remained unchanged throughout the experiment and hence acted as

an internal standard. The integral fraction of peaks was estimated as $I_a = i_a/(i_a+i_c)$, where I_a = integral fraction of 'a' peak and i_a and i_c is the intensity of the 'a' and 'c' peaks, respectively. The rate constant (k) was determined from the plot of $In(C/C_0)$ versus time, following pseudo first-order kinetics, with the rate equation, r = k[BBHM-TMB] (Figure S16). Here C = integral fraction of peak 'a' in BBHM-TMB at *time* = t and C_0 = integral fraction of the peak 'a' in BBHM-TMB at t = 0. Using these rate constants, the activation energy of the reaction was determined following the Arrhenius plot, which was found to be 77.07 kJ/mol (Figure 1d).



Scheme S1: Exchange reaction between **BBHM-TMB** and **MEE** carried out at varying temperatures in the presence of 5 mol% pTSA; the studies demonstrate the reversible exchangeability of benzyl ether.



Figure S15. Stacked ¹H NMR spectra showing the progress of the exchange reaction at 130 °C. The benzyl peak in the starting **BBHM-TMB** (peak 'a') and formed **BBMEM-TMB** (peak 'c') is highlighted (**Scheme S1**).





Figure S16: Plot of ln (C/C₀) v/s time at different temperatures of 110 °C, 120 °C, 130 °C and 140 °C. The rate constant was obtained from the slope.



Figure S17. The plot shows the variation of the ¹H NMR integral fraction of the benzyl peaks in the starting **BBHM-TMB** (peak 'a') and the formed **BBMEM-TMB** (peal 'c') with time. The reaction was carried out at 130 °C with 12 equivalents of 2-(2-methoxyethoxy)ethanol (**MEE**) (**Scheme S1**).

Study of the Mechanistic Pathways:

To study the mechanistic insights of transetherification, a model study was carried out using **BBHM**-**TMB** and phthalic anhydride (**Scheme S2a**). **BBHM-TMB** (500 mg, 1.18 mmol) was treated with phthalic anhydride (176.02 mg, 1.18 mmol) in the absence and presence of pTSA.H₂O (10 mol%) using 1.5 mL of anisole as solvent at 140 °C for 24 hours. The reaction with 10 mol % of pTSA.H₂O showed a significant change (**Figure S18**). ¹H NMR revealed the disappearance of the benzylic peak in the starting **BBHM-TMB** and the appearance of peaks corresponding to the formation of hexyl phthalate. The formation of phthalate ester confirmed the operation of a dissociative mechanism wherein alcohol resulting from the dissociation of **BBHM-TMB** converted the reactive anhydride to the corresponding phthalate ester. ESI-MS and ¹H NMR studies suggest the formation of dihexyl phthalate (**DHPT**) (**Figures S18-S19**).

To investigate the fate of carbocation in the absence of other nucleophiles, the **BBHM-TMB** was heated solely at 140 °C in the presence of 5 mol% pTSA. ¹H NMR studies revealed the generation of a new singlet peak at 4.55 ppm (peak 'a' in **Figure S20**) and the reduction of peak intensity at 4.47 pm (peak 'b' in **Figure S20**), corresponding to the benzylic peak in the starting **BBHM-TMB** molecule. The partial loss of the hexyl segment was also evident from its lowering intensity of the NMR. The peak at 4.55 ppm matches well with the benzylic peak in 4-(methyl)benzylalcohol (**Figure S20**).⁵ This suggests that formed benzylic carbocation is likely to be transformed into benzyl alcohol. Besides, the ¹H NMR reveals no noticeable change in the spectra when **BBHM-TMB** and phthalic anhydride were heated at 140 °C in the absence of the catalyst (**Figure S21**). A further control reaction was performed between phthalic anhydride and 1-hexanol at 140 °C in the presence of 10 mol% pTSA, this also suggests the formation of **DHPT** as the major product (**Figure S22**). Additionally, the phthalic anhydride was also treated with different mol % (5, 10, 20) of pTSA at 140 °C for 12 hours using anisole as solvent. The phthalic anhydride remain unreacted, as evidenced by the ¹H NMR shown in **Figure S23**, reflecting the inertness of phthalic anhydride in the given conditions.



Phthalic anhydride

Scheme S2: a) Treatment of phthalic anhydride with **BBHM-TMB** in the presence of pTSA.H₂O at 140 °C resulted in the primarily the formation of dihexyl phthalate, **DHPT**. b) Treatment of phthalic anhydride with 1-hexanol in the presence of pTSA at 140 °C resulted in the primarily the formation of **DHPT**. c) Scheme to show the inertness of phthalic anhydride in the presence of pTSA at 140 °C.



Figure S18: ¹H NMR spectra (in CDCl₃) of the product mixture obtained from phthalic anhydride and **BBHM-TMB**, which were heated in anisole at 140 °C for 12 hours in the presence of 10 mol% pTSA (**Scheme S2a**). ¹H NMR analysis suggests the primarily formation of **DHPT**.



Figure S19: ESI-MS spectrum of the mixture of **BBHM-TMB** and phthalic anhydride, which were heated to 140 °C in the presence of 10 mol % pTSA. The ESI-MS shows the presence of **DHPT (Scheme S2a)**.



Figure S20: The ¹H NMR spectra of **BBHM-TMB**, which was treated with 5 mol% pTSA at 140 °C for 3 hours. The chemical shift of the newly generated 'a' peak in BBHM-TMB matches well with the benzyl peak in the 4-(methyl)benzylalcohol.⁵ This suggests that the benzyl carbocation generated upon dissociation of **BBHM-TMB** converted into the corresponding alcohol.



Figure S21: ¹H NMR spectra (in CDCl₃) of the mixture of phthalic anhydride and **BBHM-TMB**, which were heated in anisole at 140 °C for 12 h in the absence of a catalyst.







Figure S23: ¹H NMR spectra (in CDCl₃) of phthalic anhydride, which were treated with 20 mol % of pTSA.H₂O in anisole at 140 °C for 12 h. The NMR analysis revealed the inertness of phthalic anhydride (**Scheme S2c**).

Model Studies Demonstrating the Friedel-Crafts Type Electrophilic Aromatic Substitution: This study was carried out to investigate the mechanistic insights of the ether exchange and also to show that electrophilic substitution can occur if the benzene ring is not substituted (Scheme 2b). BMM-TMB was treated with pentamethyl benzene (PMB) in the presence of 5 mol% pTSA at 140 °C for 6 hours. The ¹H NMR studies revealed the absence of the signal corresponds to the benzylic (δ ppm 4.47) and methyl ether (δ ppm 3.39) protons in the starting **BBM-TMB** and the appearance of new peaks in the region of δ ppm 4.10 corresponding to benzylic protons in the product, **PMB-TMB (Figure S24)**. The absence of the ¹H signal corresponding to the aromatic proton in the starting **PMB** also confirmed its consumption. The formation of 1-butoxy-2,4,6-trimethyl-3-(2,3,4,5,6-pentamethylbenzyl)-5-(2,3,4,6-tetramethylbenzyl) benzene (**PMB-TMB**) was further probed by ¹³C NMR and ESI-MS (**Figure S25-26)**. Thus, these model studies, in combination with the earlier discussed model studies involving phthalic anhydride, suggest the dissociative mechanism and formation of the carbocation intermediate. This model study probed the formation of carbocation type intermediate. Whereas the previously discussed model studies involving phthalic anhydride proved the formation of alcohol.

Synthesis of 1-butoxy-2,4,6-trimethyl-3-(2,3,4,5,6-pentamethylbenzyl)-5-(2,3,4,6-tetramethylbenzyl) benzene (PMB-TMB): 500 mg (1.78 mmol) BMM-TMB was taken in 25 mL RB and heated to melt at 90 °C under a nitrogen environment, followed by the addition of 5 mol % of pTSA.H₂O. PMB (3.56 mmol) was added to the reaction mixture and heated to 140 °C under a nitrogen environment for 18 hours. (Figure 2b) The product was obtained in near quantitative yield. ¹H NMR (δ ppm, CDCl₃, 400 MHz): 4.10 (s, 4H); 3.61 - 3.58 (t, 2H); 2.22 (s, 9H); 2.17 (s, 12H); 2.07 (s, 6H); 2.02 (s, 12H); 1.77 - 1.72 (m, 2H); 1.56 - 1.47 (m, 4H); 0.98-0.95 (t, 3H); 0.98 - 0.86 (t, 6H). ¹³C NMR (δ ppm, CDCl₃, 100 MHz): 154.09, 138.59, 136.29, 132.43, 132.34, 132.25, 131.24, 127.18, 72.57, 33.62, 32.49, 19.59, 17.44, 17.30, 17.07, 17.04, 14.19, 13.38. ESI-MS: Calculated for C₃₇H₅₂O (512.4015): Observed: 438.3934 [M-C₄H₉]⁺



Figure S24: ¹H NMR spectra of PMB-TMB recorded in CDCl₃.









Figure S26: ESI-MS spectrum of PMB-TMB.

Synthesis of Linear Polyether (MESTEG):

500 mg (1.78 mmol) **BMM-TMB** and 267.8 mg (1.78 mmol) trimethylene glycol were taken in a round bottom flask and purged with nitrogen. 5 mol % of pTSA.H₂O was added to it and heated at 140 °C for 24 hours with continuous stirring. Subsequently, a high vacuum was applied to favor polymerization. The linear polyether, **MESTEG** was obtained with a 91 % yield (698 mg).

¹H NMR (δ ppm, CDCl₃, 400 MHz): 4.55 (s, 81H); 3.64 (m, 293H); 3.39 (b, 3H); 2.36 (s, 54H); 2.30 (s, 108H); 1.78 – 1.74 (m, 43H); 1.54 – 1.50 (m, 44 H); 0.99 – 0.96 (t, 57).



Figure S27: The stacked ¹H NMR spectra of linear polyether, **MESTEG**, and **BMM-TMB** monomer recorded in CDCl₃. Shift in the benzyl -**CH**₂ peak from 4.47 ppm in the monomer to 4.55 ppm in the polymer, the disappearance of the peaks associated with the methyl ether in the monomer and the appearance of new peaks corresponding to triethylene glycol in the region of δ ppm 3.64 in the polymer confirm the formation of linear polyether, **MESTEG**.



Figure S28: The GPC plot of the linear polyether, **MESTEG**, obtained using THF as the eluent. GPC analysis revealed the molecular weight of **MESTEG** to be 40,800 g/mol and the polydispersity index (Đ) as 1.90. The molecular weight of the polymer was determined with respect to narrow polystyrene standards using the RI calibration method.

Synthesis of Transether Network (MESTMP)

3 g (10.69 mmol) dibenzyl ether monomer, **BMM-TMB**, was heated at 90 °C under inert conditions to melt, and 5 mol % of pTSA.H₂O were added. After 30 minutes, 961.77 mg (7.16 mmol) trimethylolpropane was added, the temperature of the reaction mixture was increased to 145 °C. The polymerization was continued for 12 hours in the nitrogen environment to obtain the transether-based network, **MESTMP**. The network was transferred by swelling it in THF. Subsequently, the network was dried under reduced pressure.



Figure S29: FT-IR spectra of the monomers, **TMP** (in black), **BMM-TMB** (in red), and network, **MESTMP** (in blue), were recorded at room temperature. The disappearance of -OH stretches of **TMP** and Ar-CH₂-O-**CH**₃ stretches of **BMM-TMB** at 2823 cm⁻¹ and 1190 cm⁻¹ in the **MESTMP** is highlighted.



Figure S30: Zoomed (500-2000 cm⁻¹) FT-IR spectra of the monomers, **TMP** (in black), **BMM-TMB** (in red), and network, **MESTMP** (in blue), were recorded at room temperature.

TGA and DSC Profile of Linear Polymer, MESTEG



Figure S31: (a) TGA profile of the linear polyether, **MESTEG**, recorded from room temperature to 600 °C with a heating rate of 10 °C/min. The temperature at which 5 % weight loss occurred was found to be 263 °C, and (b) The DSC profile of the linear polymer **MESTEG**.



Figure S32: $T_{d,5\%}$ of reported vitrimers with different chemistries.^{5–44} The dotted line represents the $T_{d,5\%}$ of **MESTMP** (292 °C), which is notably high.



Figure S33: The isothermal TGA profiles of the **MESTMP**, carried out at 185 °C (blue) and 215 °C (red) over 3 hours. The inset shows the $T_{d,5\%}$ at different times.



Figure S34: DSC thermogram of the **MESTMP**, carried out with a heating/cooling rate of 10 °C/min. The DSC studies revealed a glass transition temperature at 92 °C.



Figure S35: Stability of network **MESTMP** in n-butanol, 1-Hexanol, 1N HCl at room temperature for 60 days.



Figure S36: FT-IR spectra for the original (as synthesized) **MESTMP** (black) and the sample treated with (in red) a) hexanol, b) butanol, and c) 1 N HCl for 60 days. The samples were dried in the vacuum oven, and their FT-IR spectra were recorded. FT-IR analysis shows no significant after 60 days shows no significant change in the chemical structure after these treatments.

Table S1: Measured weight of original (as synthesized) MESTMP (initial weight) and the final weight of samples that were treated with hexanol, butanol, and 1 N HCl for 60 days. Following the treatments, the samples were dried in a vacuum oven, and their weights were recorded

Solvent	Initial Weight	Final Weight	Weight Loss (%)
Hexanol	19.7 mg	18.9 mg	4.06
Butanol	25.4 mg	25.0 mg	3.87
HCI	13.2 mg	12.8 mg	3.03



Figure S37: FT-IR spectra for the original **MESTMP** (in red) and processed **MESTMP** (in black). No significant difference in spectra of the original and processed network was observed.

Temperature (°C)	τ (s)	β Value
170	187	0.52
160	393	0.66
150	701	0.61
140	1794	0.65

$$\frac{G(t)}{G(0)} = \frac{\left(-1 * \exp\left(\left(\frac{x}{t}\right) \land b\right)\right)}{\left(-1 * \exp\left(\left(\frac{1}{t}\right) \land b\right)\right)}$$

$$\ln(\tau) = \ln(\tau_0) + \frac{E_a}{RT}$$
Eq.S2

Degradation of Linear Polymer and MESTMP Network



Figure S38: (a) Scheme showing the degradation of linear polyether (**MESTEG**), and (b) transetherbased network, **MESTMP** with excess hexanol presence of 5 mol % added catalyst (pTSA) at 140 °C.

Degradation of Linear Polymer (MESTEG) and Network (MESTMP): 100 mg linear polyether **MESTEG** was taken in excess of dried 1-hexanol (2 mL) and heated at 140 °C for 24 hours in the presence of 5 mol % of catalyst pTSA.H₂O. Then, the excess of 1-hexanol and formed triethylene glycol was removed under high temperature and low pressure to obtain the **BBHM-TMB** monomer with a yield of 79 %. Similarly, 100 mg of network **MESTMP** was degraded in the presence of excess of 1-hexanol (2mL) and 5 mol % of pTSA at 140 °C.



Figure S39: ¹H NMR (CDCl₃) spectra of **BBHM-TMB**, recovered after degradation of the linear polymer, **MESTEG**.

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